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Optical parameters of spun on films of Calix-4-resorcinarene molecules by attenuated total reflection technique

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Abstract : Surface plasmon resonance (SPR) measurements under attenuated total reflection (ATR) were taken in air as well as in pure water, for an overlayer containing Calix-4-resorcinarene (Azo1) molecules spun on Au coated slides. SPR data for both media used throughout this work were fitted to Fresnel reflection theory for a four layered (glass-Au-Azo1-air or water) system. By varying the Azo1 film thickness during the fitting procedure, different solutions have been obtained for the film dielectric constant and hence its refractive index. The refractive index *versus* thickness for both media were plotted and from the intersecting point of the two curves an exact solution was found which gives film optical parameters of organic overlays.

Keywords : Refractive index, dielectric constant, thickness, attenuated total reflection.

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1. Introduction

Surface Plasmons (SP) are very elementary excitations of metal-dielectric interfaces. The dispersion relation of the SP is obtained by solving Maxwell's equations with special boundary conditions, such as the finite thickness of the metal and the dielectric constant. To allow the excitation of the surface plasmons oscillations the real part $\varepsilon_1(\omega)$ of the dielectric function $\varepsilon(\omega)$ has to be negative and the imaginary part $\varepsilon_2(\omega)$ should be very small, a condition which is fulfilled in metal. The SP are bounded to the surface due to the parallelism of the real part of the wavenumber vector $\boldsymbol{K}_{sp}$ to the metal-air interface. Since the K vector of the SP ($\boldsymbol{K}_{sp}$) is always larger than the light wave vector K in air, surface plasmons can only be excited *via* coupling mechanism. This method relies on the excitation of the surface plasmon oscillation (SPO) at a metal air interface. It may be applied for the characterization metal film [1] as well as organic over layer over the metal film. The light characterized by ω, K and θ, has to travel from the prism to the metal air interface to excite the SPO. Two approaches are possible : (1) Excitation *via* an air gap (Otto arrangement [2]), (2) Excitation *via* metal film (Kretshmann arrangement [3]). In both cases the light tunnels through a medium from the base of the half cylinder to the metal air interface, in the former it is the air gap and in the latter, the metal film itself. The weak coupling between the exciting beam and the resonant electron plasma allows the built up of a strong SPO with resonant enhancement of the electric field at the surface. This resonance causes an enhanced absorption. As a result of this increased absorption, the reflection drops dramatically; under optimum condition it becomes less than 5%. This decrease in reflectivity is called attenuated total reflection (ATR). To obtain such a sharp and deep minimum, the damping of resonance has to be small. The damping is given by both the extinction of the metal and the coupling between exciting beam and SPO. Optimum resonance is obtained if the both damping mechanisms are equal. This is known as surface plasmon resonance (SPR) technique with ATR. The resulting curve under resonance condition showing minimum reflectivity is SPR curve.

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This paper attempts to obtain the optical parameters of Calix-4-resorcinarene (Azo1) molecules spun on Au coated slides. SPR data for both media used throughout this work were fitted to Fresnel reflection theory for a four layered (glass-Au-Azo1-air or water) system. By varying the Azo1 film thickness during the fitting procedure different solutions have been obtained for the film dielectric constant and hence its refractive index. The refractive index *versus* thickness for both media were plotted and from the intersecting point of the two curves an exact solution was found which gives film optical parameters of organic overlayers.

2. Optical constants spun azol layer

The value of the reflection coefficient of the four layered system as shown in the Figure 1 follows from the Fresnel equations for P-Po-larized light [4] which can be written as

$$R_{1234} = |r_{1234}|^2,$$

$$r_{1234} = \frac{n_{234} + z_{234} r^{-1}{}_{12} \exp(2iK_{z2}d_2)}{n_{234} + z_{234} r_{12} \exp(2iK_{z2}d_2)} r_{12}, \quad (1)$$

$$r_{234} = \frac{z_{23}n_{34} + z_{34}n_{23}\exp(2iK_{z3}d_3)}{n_{23}n_{34} + z_{23}z_{34}\exp(2iK_{z3}d_3)} \equiv \frac{z_{234}}{n_{234}}, \quad (2)$$

$$r_{ij} = \frac{{}_jK_{zi} - {}_iK_{zj}}{{}_jK_{zi} + {}_iK_{zj}} \equiv \frac{z_{ij}}{n_{ij}}. \quad (3)$$

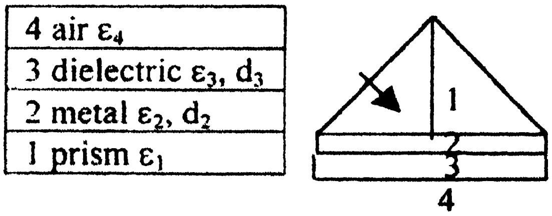

Figure 1 Schematic diagram showing the Kretchmann configuration of prism-gold-air-calix-air system.

Shifts in K_{min} and the resonance angle θ_{air} due to overlayer in contact with air due to the presence of layer 3 are given by

$$\Delta K_{min} = d_3\left(\frac{2\pi}{\lambda}\right)^2 \frac{(\varepsilon_r\varepsilon_4)^{1/2}(\varepsilon_3\varepsilon_r - \varepsilon_3\varepsilon_4 - \varepsilon_4\varepsilon_r + \varepsilon_3^2)}{\varepsilon_3(\varepsilon_r^2 - \varepsilon_4^2)(\varepsilon_r - \varepsilon_4)}, \quad (4)$$

$$\Delta\theta_a = \frac{(2\pi/\lambda)(|\varepsilon_2|\varepsilon_4)^{3/2} d}{n_p \cos\theta(|\varepsilon_2| - \varepsilon_4)^2 \varepsilon}(\varepsilon - \varepsilon_4). \quad (5)$$

A similar expression can be derived for the shift $\Delta\theta_w$ in resonance angle due to the over layer in contact with water

3. Deposition technique

For SPR measurement, gold films of approximately 40 to 50 nm thick are deposited on ultrasonically cleaned glass slides by thermal evaporation under vacuum of 10^{-6} Torr at the evaporation rate of 1 nm s^{-1}. Gold-coated glass slides are vacuum held onto the rotating chuck of a photo resist spinner model 4000 from electronic micro system and the speed of rotation was varied from 1000–6000 rpm (Figure 2). A small amount of Calix-4 resocinarence (Azo1) compounds solution of certain concentration was allowed to fall on the rotating substrate from a micro syringe and the film spinning continued for a period of 15 seconds. The thickness of each film depends on spinning speed and solution concentration [5].

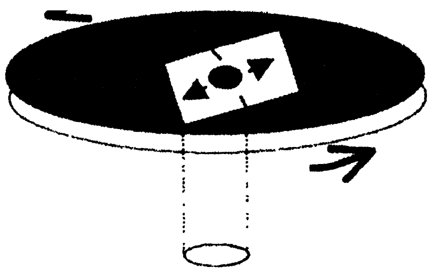

Figure 2. Schematic diagram of a spin coater.

4. Characterisation

For finding the dielectric constant and thickness of Azol overlayer, we need additional independent data to do a separate determination of ε_3 and d_3. It is apparent from eq. (5) that both d and ε cannot be determined independently from $\Delta\theta_a$ alone with some degree of accuracy. SPR measurements in two dielectric media of different indices have therefore been utilised as an effective method for simultaneous determination of film thickness and refractive index of spun Azo1 molecules with a high degree of accuracy. Two media we have taken are air and water respectively. The variation of the refractive index n of the spun film obtained from the fitting procedure as a function of its thickness d for film combination in contact with air and water are plotted in Figure 3. Applying eq. (5) to the point of intersection for two $n(d)$ curves, for the SPR curves measured in two different media, the complex dielectric

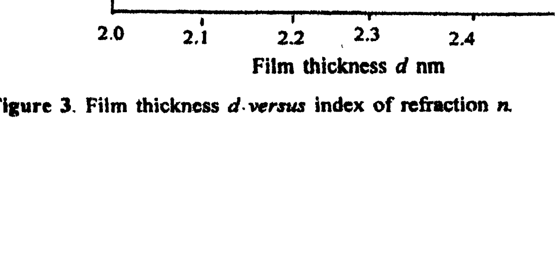

Figure 3. Film thickness *d versus* index of refraction *n*.

constant ε can be found. Thin films of Azo1 molecules are transparent at 633 nm, and, as excepted, the imaginary part of the dielectric constant is infinitely small. The part n of refractive index of Azo1 films is found to be 1.494 from the knowledge that $n = (\varepsilon)^{1/2}$.

5. Conclusion

The thickness and refractive index of (Azo 1) spun films have been accurately obtained by using SPR measurements in two dielectric media. These optical parameters are very essential for process control in thin film technology. This optical SPR method offer the advantage of being noncontact, nondestructive, fast, precise, sensitive and reproducible.

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